Indian J. Phys. **47**, 65–68 (1973)

Partition and approach to equilibrium

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(*Received* 19 *February* 1972, *revised* 26 *April* 1972)

In this paper the statistical evolution and also the approach to equilibrium of a thermodynamic system have been studied from an information-theoretic consideration.

Introduction

We consider a system immersed in a reservoir, which may be assumed to be a part of a large ideally closed system Interaction between the part-systems leads to the establishment of statistical equilibrium over the whole large system, while equilibrium in a part-system is established by its internal interactions. From molecular-statistical point of view the whole system is a collection of a large number of interacting components (molecules). Let x represent the energy of a component and E that of the system under consideration. Due to interaction both x and E are random fluctuating quantities The total energy E of the system can be considered as a statistic, that is, a function of x, say $T(x)$ in the sample space (which we shall call here the energy space) of x. Let p_i and P_k be the micro- and macro-states distribution of the random variables x and E, respectively, while p_i^0 and P_k^0 are the corresponding initial guesses. As regards the equilibrium of the system under consideration, the only available information we have, is that the average value of the energy of the system $\sum_i p_i T(x_i) = \overline{E}$ is known. (Katz 1967).

The problem, as in statistical mechanics, is to make the best guess p_i for equilibrium on the basis of the available information and for this we shall make use of Kullback minimum discrimination information theorem (Kullback 1961), which is analogous to maximum-entropy principle ((Jaynes 1957a). Kullback discrimination information in favour of p_i against p_i^0 is given by $\sum_i p_i \ln p_i/p_i^0$.

In case when p_i^0's are each equal to a constant such that $\sum_i p_i^0 = 1$, then $\sum_i p_i \ln p_i/p_i^0$ reduces to $\sum_i p_i \ln p_i$ except for an additive constant. But this is nothing but the negative of Shannon's measure of entropy whose identification with the entropy of statistical mechanics is well-known (Jaynes 1957b).

The minimum value of $\sum_i p_i \ln p_i/p_i^0$ subject to the condition that $\sum_i p_i T(x_i) = \overline{E}$ is

$$H(\overline{E}, \lambda) = \lambda\overline{E} - \ln \phi(\lambda) \qquad \dots \quad (1)$$

and this is possible if and only if

$$p_i = \exp(\lambda T(x_i))p_i^0/\phi(\lambda)$$

where $$\bar{E} = \frac{d}{d\lambda}\ln\phi(\lambda), \quad \phi(\lambda) = \sum_i \exp(\lambda T(x_i))p_i^0$$

As regards the equilibrium of the system we should mention as pointed out by Ehrenfest (1959) that equilibrium is to be conceived in such 'coarse-grained' sense as corresponds to the maximum possible uniformity of distribution without any loss of available information and which from statistical point of view is equivalent to the minimal sufficient partitioning of the sample space (energy-space) of the system. (Chakrabarti 1972).

Partition and Approach to Equilibrium

As a system approaches equilibrium, as it grows old and as the equilibrium is to be conceived in the 'coarse-grained' sense with maximum possible uniformity of distribution, the approach to equilibrium would be through the process of 'coarse-graining' or through the partitioning of the energy space of the system.

In the process of minimization of $\sum_i p_i \ln p_i/p_i^0$ we note that (Kullback 1961)

$$\sum_1 p_i \ln \frac{p_i}{p_i^0} \geqslant \sum_k^* P_k \ln \frac{P_k}{P_k^0} \geqslant H(\bar{E}, \lambda) \qquad \dots (2)$$

where the summations Σ and $\Sigma^*$are for the 'fine-grained' and 'coarse-grained' distributions, respectively. The first member of the inequality (2) is in general greater than the second and this is due to the 'coarse-graining' of the 'fine-grained' distribution (equivalently 'coarse-grained' partitioning of the energy-space) and this loss of information corresponds to the process of irreversibility (Katz 1967, Jaynes 1957b). The equilibrium itself is achieved when $\sum_i p_i \ln p_i/p_i^0$ assumes its minimum value $H(\bar{E}, \lambda)$ by discarding all other informations as obsolete and partaining as given information, only the average value of the total energy $\sum_i p_i T(x_i) = \bar{E}$, which is the only available information as regards the equilibrium state of the system under consideration. The equilibrium in fact, in the information-theoretic approach to statistical mechanics, can be defined as the situation in which the averages of the constants of motion (here the average energy) are the only knowledges or informations available (Katz 1967). In this spirit, the evolution of the system undergoing irreversible processes and approaching equilibrium would be evident, if we can show for the random motion of the system the gradual decrease of $\sum_i p_i \ln p_i/p_i^0$ with time regardless of any other considerations.

For this we consider the behaviour of $\sum_i p_i \ln p_i/p_i^0$ with respect to the random motion of the system. The time evolution of the microstate distribution $p_i(t_1)$ at time t_1 into another $p_j(t_2)$ at a later time t_2 ($t_2 > t_1$) can be written in the form

$$p_j(t_2) = \sum_j p_{ij} p_i(t_1) \tag{3}$$

where p_{ij} is the transition probability from i-th state to j-th state and satisfies the conditions

$$p_{ij} \geqslant 0 \quad \text{and} \quad \sum_j p_{ij} = 1.$$

p_{ij} in general depends on the memory of the system and also on the initial state.

If the prior probability distribution p_i^0 also follows the same time evolution as that of p_i in (3) that is, if

$$p_j^0(t_2) = \sum_i p_{ij} p_i^0(t_1), \tag{4}$$

then it can be shown with the help of (3) that

$$\sum_j p_j(t_2) \ln \frac{p_j(t_2)}{p_j^0(t_2)} < \sum_i p_i \ln \frac{p_i(t_1)}{p_i^0(t_1)}, \qquad t_1, \tag{5}$$

which means that due to the smoothing of the distribution by the relation (3), the discrimination information $\sum_i p_i \ln p_i/p_i^0$ will decrease gradually with time and this degradation of information (in which lies the true meaning of irreversibility) with time implies the gradual approach of the system to equilibrium and this is nothing but the irreversible approach to equilibrium.

Finally we note that our model, with arbitrary initial distribution, will approach the canonical distribution; in fact it follows from the equality of the last two members of the inequality (2), which in the case of equilibrium becomes although an equality.

For $\overset{*}{\Sigma}_k P_k \ln \dfrac{P_k}{P_k^0} = H(\overline{E}, \lambda)$, if P_k is given by (Kullback 1961)

$$P_k = \exp(\lambda E_k) P_k^0/\phi(\lambda) \tag{6}$$

which is Gibbs' canonical distribution of energy E_k with $\lambda = -1/kT$, k being Boltzmann constant, T, absolute temperature, and P_k^0 is the weight for the state with energy E_k.

Conclusion

In conclusion it should be mentioned that in our method of approach, no special assumptions are made concerning the structure of the system. In particular, no considerations from the kinetic theory have been taken for the study of the time-evolution of the system.

ACNOWLEDGEMENTS

The author wishes to thank Dr. M. Dutta, University of Calcutta, for advice in preparation of this note He also offers his thanks to the referee of the paper for some valuable comments

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